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THE ELECTRODEPOSITION OF LOW CONTRACTION CHROMIUM/MOLYBDENUM ALLOYS USING PULSE-REVERSE PLATING

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DECEMBER 1994

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13. ABSTRACT *(Maximum 200 words)*

The use of modulated pulse periodic reverse (pulse-reverse) current to electrodeposit a low contraction (LC) chromium/molybdenum alloy has been evaluated. When using one full pulse-reverse plating cycle, the percent molybdenum in the deposit increased almost 400 percent (from 1 to 4 percent) as the current in the reverse cycle was increased from 0 to 10 amps. However, when the pulse-reverse current was carried to six full plating cycles, the percent molybdenum in the deposit was not dependent upon the current and remained constant at about 1 percent. This is about the same percent molybdenum that could be expected in direct current-plated LC chromium/molybdenum alloy and about half the percent molybdenum that could be expected in an on/off pulse-plated LC chromium/molybdenum alloy.

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Molybdenum, Chromium, Electroplating, Electrodeposition, Pulse, Pulse-Reverse

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TABLE OF CONTENTS

List of Illustrations

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INTRODUCTION

The usefulness of existing high contraction (HC) chromium electrodeposits as well as future low contraction (LC) chromium electrodeposits is limited by the thermal resistance and the reactive environment found when using newer, high energy propellants. In addition, aqueous electrodeposition of refractory metals has typically been limited to just one metal--chromium (with a melting temperature of 1875°C). Therefore, the usefulness of both the present HC chromium and the future LC chromium coatings can be enhanced by raising their melting temperature by alloying them with other high melting temperature refractory metals such as molybdenum (with a melting temperature of 2600°C).

In addition, a chromium/molybdenum alloy electrodeposit is very desirable because of its reported benefits including improved wear, corrosion, and erosion resistance over conventional chromium deposits (refs 1-3). Yuan et al. have found that a chromium/molybdenum alloy electrodeposit possessed better tribological characteristics than pure chromium electrodeposits (ref 4). Brenner (ref 5) has reported that the chromium/molybdenum alloy did not have the network of cracks characteristic of the unalloyed chromium deposit and, in addition, the chromium/molybdenum codeposit lasted from three to eight times longer in wear tests than pure chromium deposits.

The molybdenum content in an aqueously deposited chromium/molybdenum alloy is usually quite low--no more than 1 percent. Investigators such as Ma (ref 6) claimed to have obtained chromium/molybdenum alloy deposits with molybdenum contents as high as 22 percent. However, attempts by Brenner (ref 5) and Holt (ref 7) to duplicate Ma's results were unsuccessful. More recent attempts to aqueously electrodeposit a direct current (dc)-plated chromium/molybdenum alloy with molybdenum contents higher than 1 percent have been unsuccessful (ref 8).

Molybdenum concentrations as high as 2.4 percent were obtained in an LC chromium/molybdenum alloy when unipolar (on/off) pulse current was used instead of straight dc current (ref 9). However, this is still not enough molybdenum to improve the thermal resistance or significantly improve the mechanical properties of the alloy. Recognizing the need to improve the molybdenum content beyond 2.4 percent, the use of pulse-reversing current was investigated.

EXPERIMENTAL PROCEDURE

The experimental procedure was carried out exactly as described in a previous report (ref 9) except for the electrodeposition process. Pulse reversing current was used instead of on/off pulse current. The LC Cr/Mo alloy was deposited using either one pulse-reverse cycle (total plating time 1350 seconds) or six pulse-reverse cycles (total plating time 8100 seconds). Each forward part of a pulse-reverse cycle consisted of a total time of 900 seconds (broken into 90 ms/90 ms on/off pulses). Each reverse part of a pulse-reverse cycle consisted of a total time of 450 seconds (broken into 1 ms/1 ms on/off pulses).

The current used for the forward part of a pulse-reverse cycle was kept constant at 10 amps (or 100 A/dm^2). The current used for the reverse part of each pulse-reverse cycle was varied from 0 to 10 amps. The variation of the molybdenum content with increasing current during the reverse part of a cycle was evaluated.

RESULTS

The experiment was divided into two parts. In the first part, only one pulse-reverse cycle was used (for a total plating time of 1350 seconds). The current used for the reverse part of the cycle was varied from 0 to 10 amps (0 to 100 A/dm^2). When the current for the reverse part of the cycle was at 0 amps, the molybdenum content in the LC chromium/molybdenum alloy was about 1 percent. The percentages are only approximations due to the limitations of doing quantitative measurements with energy dispersive x-ray analysis (EDAX). The results are shown in Figure 1. It is also obvious here that when the pulse-reverse cycle has 0 amps for the reverse current, the current profile resembles an on/off forward pulse.

Next, the reverse current was increased to 1 amp and the molybdenum content increased to about 2 percent. The results are shown in Figure 2. When the reverse current was then increased to 5 amps, the molybdenum content of the LC chromium/molybdenum alloy again increased--to about 3 percent (Figure 3). Finally, when the reverse current was increased to 10 amps, the percent molybdenum in the alloy increased to 4 percent. These results are shown in Figure 4. The plating thicknesses at these short pulse-reverse plating times never exceeded 5 μm. This thickness is inadequate for gun-tube coatings which typically are 125 μm thick.

However, the rise in the molybdenum content from 1 to 4 percent as the current in the reverse part of the cycle was increased from 0 to 10 amps is considered significant. Since the forward part of the cycle remained unchanged for this part of the experiment, this finding suggests that at higher reverse currents more chromium than molybdenum is being removed during the reverse part of the cycle. As a result, it could be concluded that it may be possible to increase the overall percent molybdenum beyond 4 percent simply by carrying out the plating times for several hours.

In the second part of the experiment, six pulse-reverse cycles were used in an effort to determine if the percent molybdenum in the chromium/molybdenum deposit could be increased beyond 4 percent simply by plating at longer times. The total plating time for the six pulse-reverse cycles was 8100 seconds. The current profile was identical to the first part of the experiment except that six pulse-reverse cycles were used instead of one.

The current used for the reverse part of each cycle was again varied from 0 to 10 amps. The results are shown in Figure 5. Unlike part one of the experiment, the molybdenum content of the chromium/molybdenum alloy did not increase as the reverse current was increased from 0 to 10 amps. The molybdenum content remained basically unchanged at about 1 percent. This observation leads to the conclusion that when using longer plating times (times long enough to get a deposit of at least 25 μm), the molybdenum content of a chromium/molybdenum alloy cannot be improved beyond 1 percent when plating with pulse-reverse current.

CONCLUSIONS

The use of modulated pulse periodic reverse (or pulse-reverse) current was compared to dc and on/off pulse current with respect to increasing the molybdenum content of a aqueously plated chromium/molybdenum alloy. When using short plating times (one pulse-reverse cycle with a total plating time of 1350 seconds), a maximum molybdenum concentration of 4 percent was obtained. This compares to a maximum molybdenum concentration of 1 percent for dc-plated chromium/molybdenum alloys and 2.4 percent for on/off pulse-plated chromium/molybdenum alloys. However, the plating thicknesses at these short pulse-reverse plating times are inadequate (less than 5 μm) for gun-tube coatings which are typically 125 μm thick.

However, when six pulse-reverse cycles were used (in an effort to deposit thicker coatings), the maximum molybdenum concentration of the alloy was only 1 percent. This percentage is comparable to dc-plated chromium/molybdenum alloys and is significantly less than the 2.4 percent molybdenum obtained when using on/off pulse current.

REFERENCES

1. P. Fenton and A. Oolbekkink, Diesil Engineers and Users Association, June 1973.

2. K. S. Indira and B. Shenoi, "Electrodeposition of Chromium-Molybdenum Alloys," *Metal Finishing*, Vol. 63, 1965, pp. 56-79 and 94-97.

3. K. Aotani an K. Nistimoto, *J. Metal Finishing Society of Japan*, Vol. 21, No. 7, 1970, p. 356.

4. F. Bing, X. Fang, G. Wenzhen, Z. Yuan, and L. Yunfeng, "Tribological Characteristics of Cr-Mo Dispersed Electrodeposits," *Proceedings of the JSLE International Tribology Conference*, Tokyo, Japan, 1985.

5. A. Brenner, *Electrodeposition of Alloys*, Vol. II, 1st Ed., Academic Press, Inc., New York, 1963, p. 113.

6. Chuk Ching Ma (for Westinghouse Electric Corp.), "Electroplating of Chromium-Molybdenum Alloys," U.S. Patent No. 2526227, 1950.

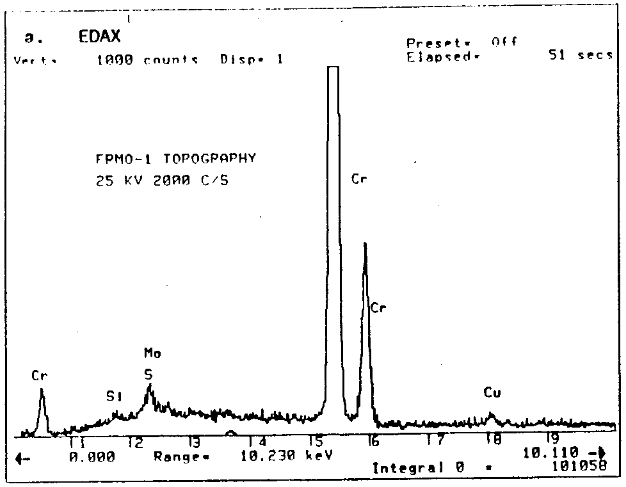
7. M.L. Holt, "Less Common Metals and Alloys, Electrodeposition From Aqueous Solutions," *Metal Finishing*, Vol. 54, 1956, pp. 48-55.

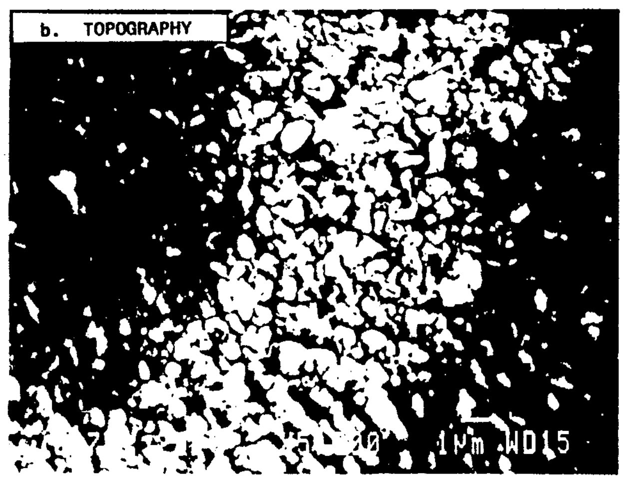
8. Y.V. Pozdeeva, M.A. Shluger, and L.D. Tok, "Effect of Molybdate Ions on Electrodeposition of Chromium," *Prot. Met.*, Vol. 16, No. 3, March-April 1980, pp. 278-280.

9. Mark D. Miller and Stephen Langston, "Chromium/Molybdenum Alloy Plating Part I: The Electrodeposition of Low Contraction Chromium/Molybdenum Alloys Using Unipolar (On/Off) Pulse Plating," ARCCB-TR-94011, March 1994.

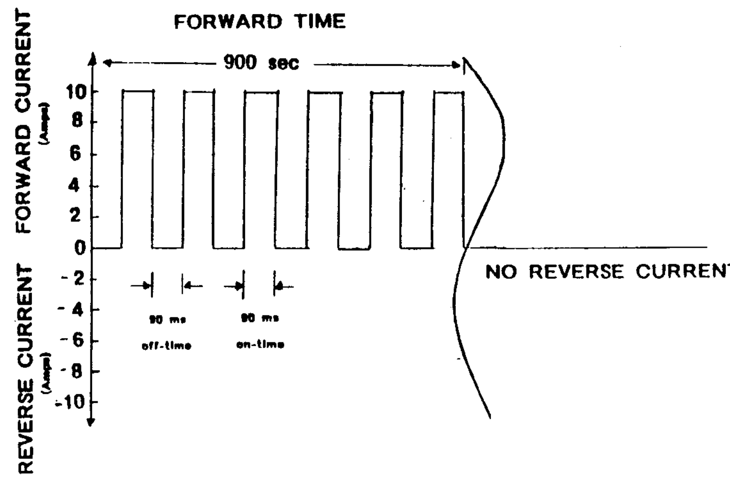
PULSE - REVERSING STUDY (with Cr/Mo)

ONE FULL CYCLE (900 sec foward/450 sec reverse)
TOTAL PLATING TIME - 1350 sec (one full cycle)
REVERSE CURRENT: 0 Amps





PULSE - REVERSING STUDY (WITH Cr/Mo)
VARIATION IN REVERSE CURRENT



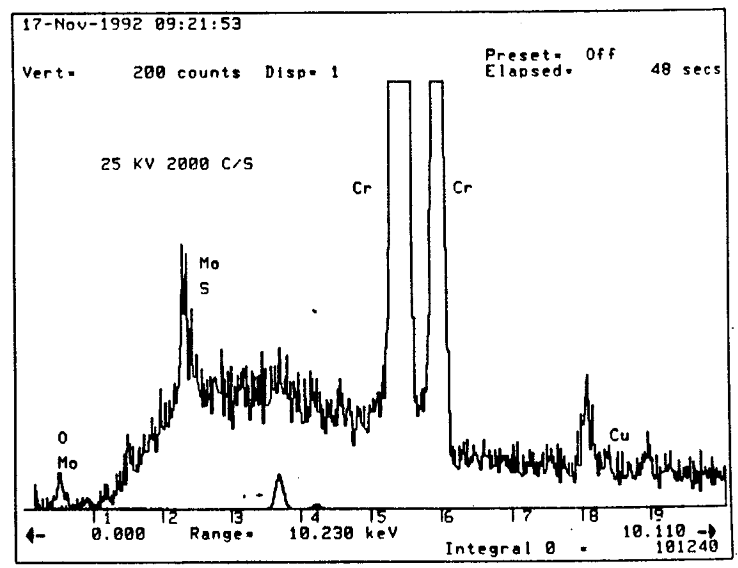


Figure 1. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 0 amps on the reverse current) was used.

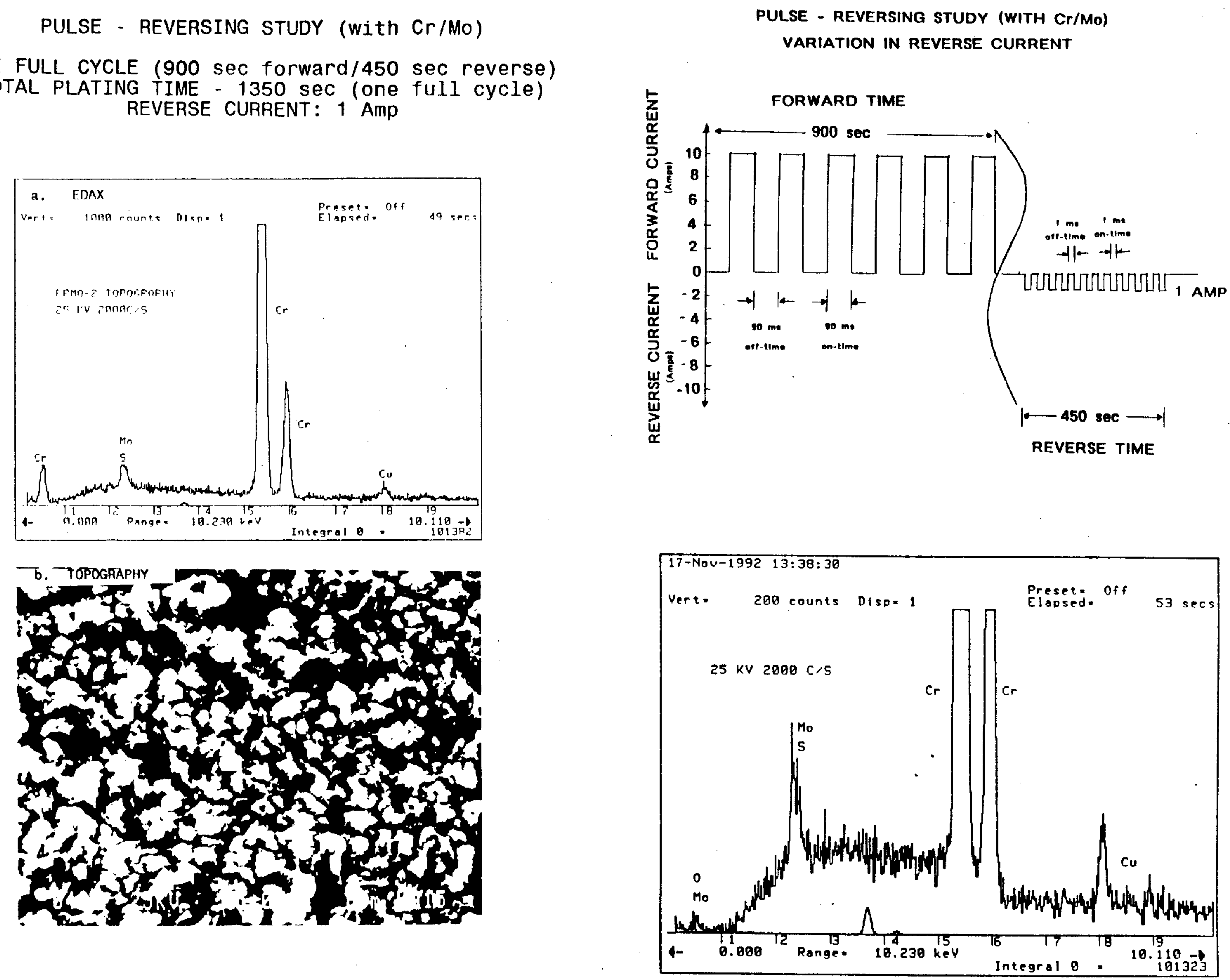
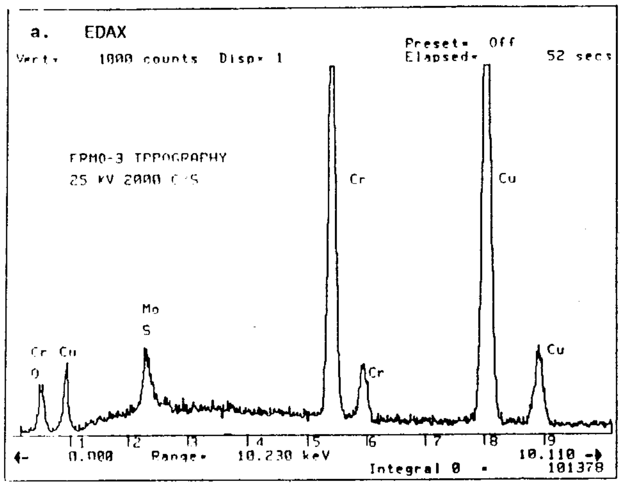
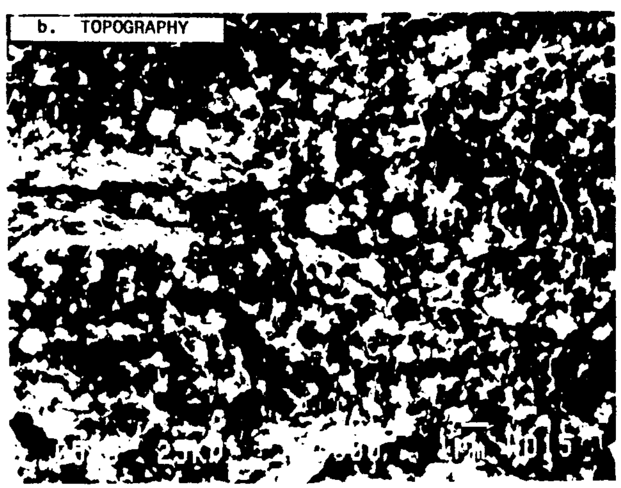


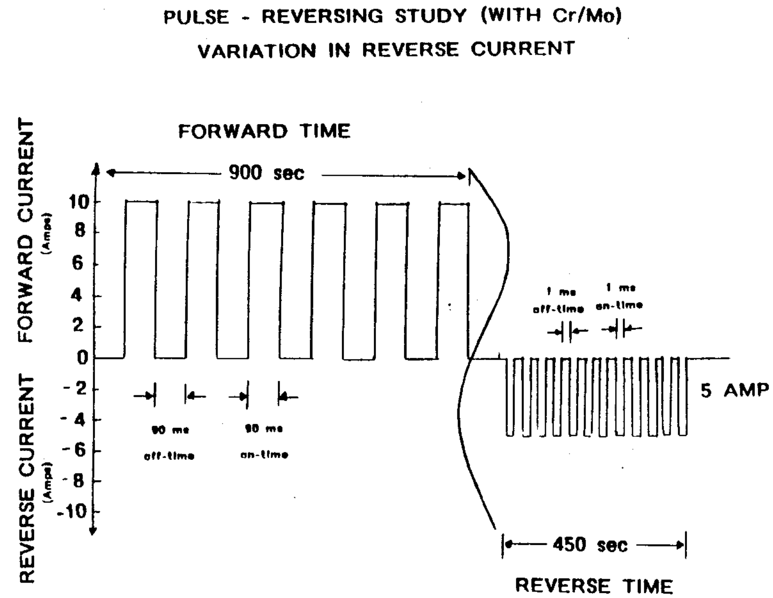
Figure 2. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 1 amp on the reverse current) was used.

PULSE - REVERSING STUDY (with Cr/Mo)

ONE FULL CYCLE (900 sec forward/450 sec reverse)
TOTAL PLATING TIME - 1350 sec (one full cycle)
REVERSE CURRENT: 5 Amps







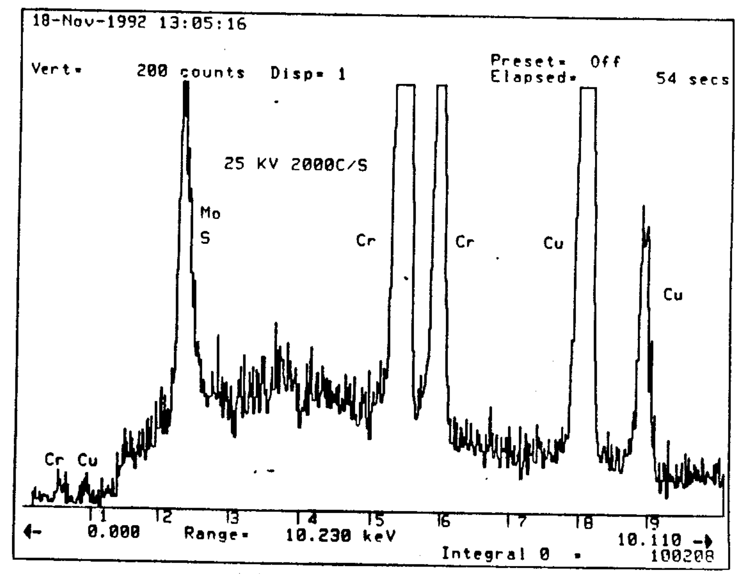


Figure 3. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 5 amps on the reverse current) was used.

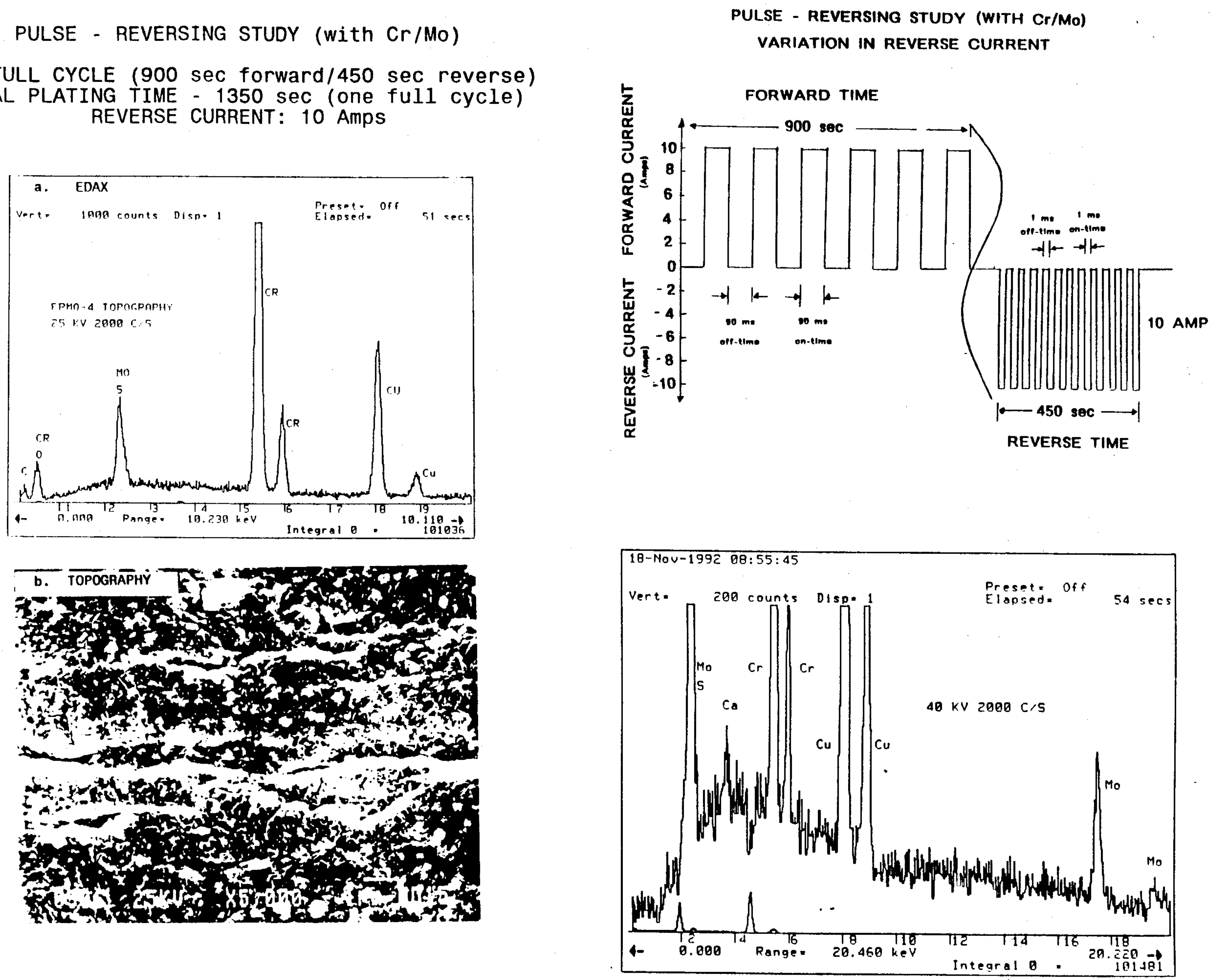
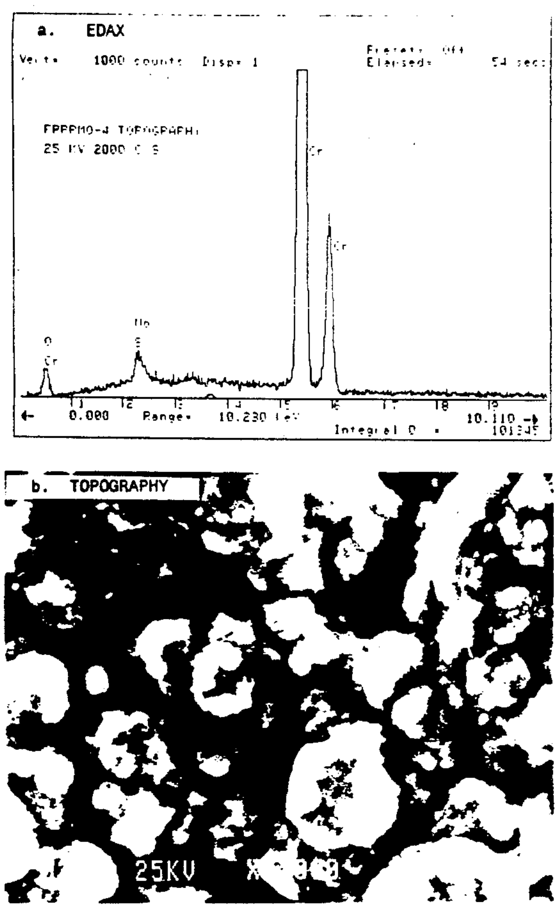
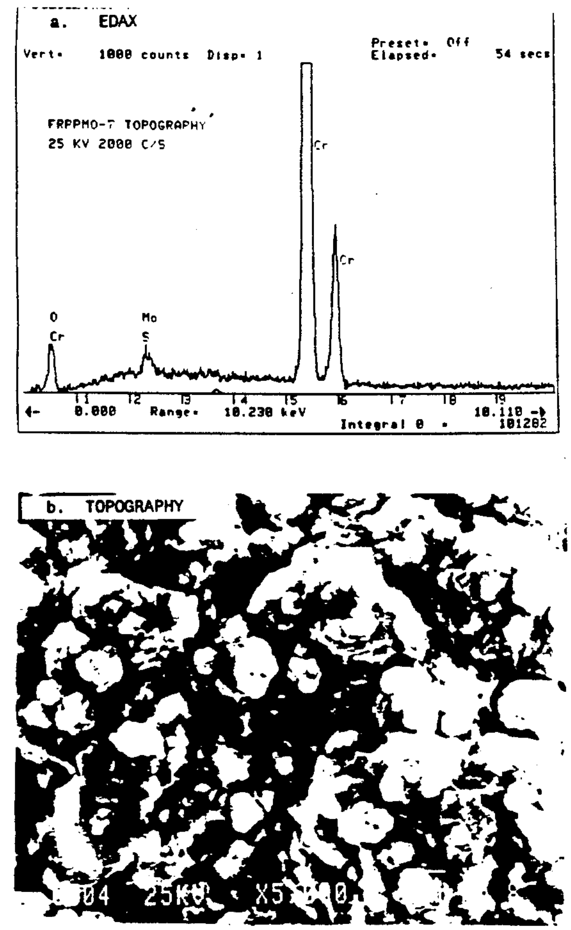


Figure 4. The EDAX (using two different instruments) and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. One pulse-reverse cycle (with 10 amps on the reverse current) was used.

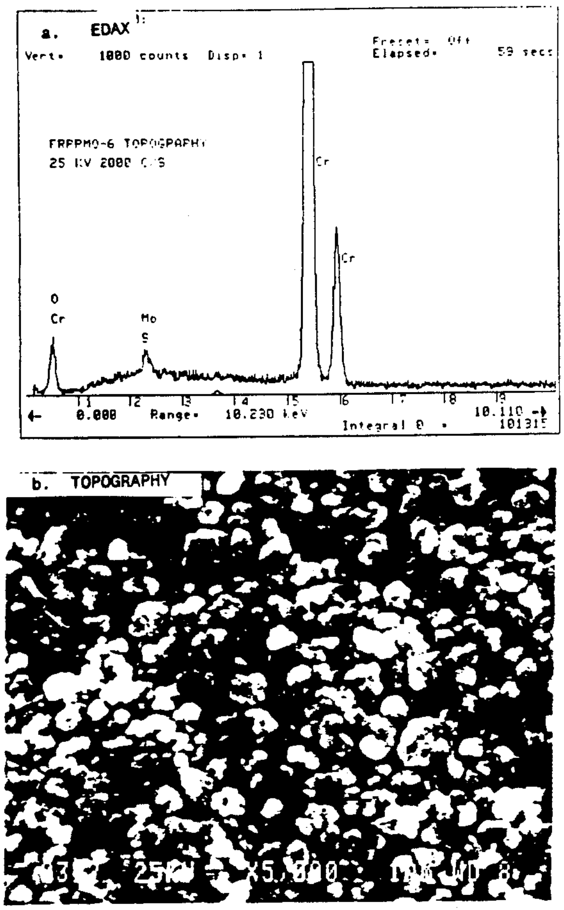


Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 0 Amp

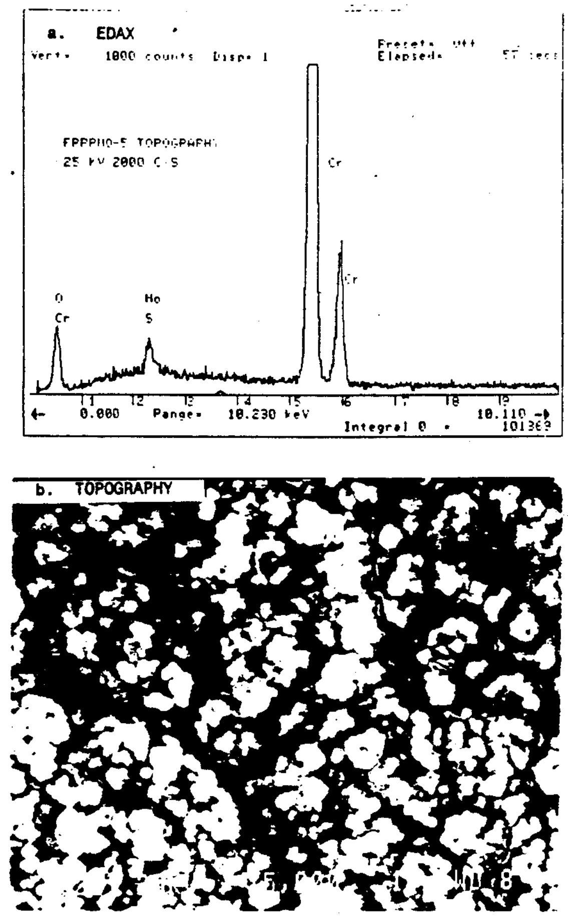


Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 1 Amp

Figure 5. The EDAX and the topography of an LC Cr/Mo alloy and the current profile used to deposit the alloy. Six pulse-reverse cycles (with 0, 1, 5, and 10 amps on the reverse current) were used.



Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 5 Amps



Pulse-Reversing Study (with Cr/Mo)
One full cycle (900 sec forward/450 sec reverse)
Total plating time - 8100 sec (six full cycles)
Reverse current: 10 Amps

Figure 5. Continued.

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